

**UTILITY PATENT
APPLICATION TRANSMITTAL**

(Only for new nonprovisional applications
under 37 CFR 1.53(b))

Attorney
Docket No.

H000010

Total
Pages

First Named Inventor or Application Identifier

Jung Chuan CHUO; Jung Lung CHIANG

Express Mail Label No.

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APPLICATION ELEMENTS FOR:

**A-WO₃-GATE ISFET DEVICES AND METHOD OF
MAKING THE SAME**

ADDRESS TO: Assistant Commissioner for Patents
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1. ☒ Fee Transmittal Form (Incorporated within this form)
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2. ☒ Specification Total Pages **[25]**
3. ☒ Drawing(s) (35 USC 113) Total Sheets **[6]**
4. ☒ Oath or Declaration Total Pages **[2]**
 - a. ☒ Newly executed (original or copy)
 - b. ☐ Copy from prior application (37 CFR 1.63(d)
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 - i. ☐ Deletion of Inventor(s)
Signed statement attached deleting inventor(s) named in prior application,
see 37 CFR 1.63(d)(2) and 1.33(b).
5. ☐ Incorporation by reference (useable if box 4b is checked)
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under box 4b, is considered as being part of the disclosure of the accompanying application and is incorporated by reference therein.
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7. ☐ Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
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ACCOMPANYING APPLICATION PARTS

8. ☒ Assignment Papers (cover sheet and document(s))
9. ☐ 37 CFR 3.73(b) Statement (when there is an assignee) ☒ Power of Attorney

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10. ☐ English translation Document (if applicable)

11. ☐ Information Disclosure Statement ☐ Copies of IDS Citations

12. ☐ Preliminary Amendment

13. ☒ Return Receipt Postcard (MPEP 503)

14. ☒ Small Entity Statement(s) ☐ Statement filed in prior application
Status still proper and desired.

15. ☐ Claim for Convention Priority ☐ Certified copy of Priority Document(s)

a. Priority of ____ application no's. ____ filed on ____ is claimed under 35 USC 119. The certified copies/copy have/has
been filed in prior application Serial No. ____.
(For Continuing Applications, if applicable)

16. ☐ Other _____

17. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

☐ Continuation ☐ Division ☐ Continuation-in-part (CIP) of prior application no. ____/____

FEE TRANSMITTAL	Number Filed	Number Extra	Rate	Basic Fee \$690.00
The filing fee is calculated below				
Total Claims	39 - 20	19	x \$18.00	342.00
Independent Claims	3 - 3	0	x \$78.00	
Multiple Dependent Claims			\$260.00	
Basic Filing Fee				1,032.00
Reduction by 1/2 for small entity				516.00
Fee for recording enclosed Assignment			\$40.00	40.00
TOTAL				556.00

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☒ A check in the amount of \$ 556.00 is enclosed to cover the filing fee of \$516.00 and the assignment recordation fee of \$40.00.

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RJH

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Applicant or Patentee: Jung Chuan CHOU and Jung Lung CHIANG

Attorney's

Serial or Patent No.: _____

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For: a-WO₃-GATE ISFET DEVICES AND METHOD OF MAKING THE SAME

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY
STATUS (37 CFR 1.9(f) and 1.27 (d)) - NONPROFIT ORGANIZATION**

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF ORGANIZATION National Yunlin University of Science and Technology

ADDRESS OF ORGANIZATION 123, Sec. 3, University Rd., Touliu, Yunlin, Taiwan
640, R.O.C.

TYPE OF ORGANIZATION

☒ UNIVERSITY OR OTHER INSTITUTION OF HIGHER EDUCATION

☐ TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 USC 501(a) and 501(c)(3))

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I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for purposes of paying reduced fees under section 41(a) or (b) of Title 35, United States Code with regard to the invention entitled a-WO₃-GATE ISFET DEVICES AND METHOD OF MAKING THE SAME by inventor(s) Jung Chuan CHOU and Jung Lung CHIANG described in

☒ the specification filed herewith

☐ application serial no. _____, filed _____

☐ patent no. _____, issued _____

I have declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above identified invention.

If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(d) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities (37 CFR 1.27)

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I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Jung Chuan CHOU

TITLE IN ORGANIZATION Dean

ADDRESS OF PERSON SIGNING 123, Sec. 3, University Rd., Touliu, Yunlin, Taiwan
640, R.O.C.

SIGNATURE Jung Chuan Chou DATE February 29, 2000

Jung Lung Chiang DATE February 29, 2000

TITLE OF THE INVENTION

a-WO₃-GATE ISFET DEVICES AND METHOD OF MAKING THE SAME

BACKGROUND OF THE INVENTION

5

Field of the invention:

The invention relates to an ion sensitive field effect transistor (ISFET), and in particular relates to an a-WO₃-gate ISFET fabricated by RF-sputtering for detecting the
10 hydrogen ions in aqueous solution. In addition, this invention relates to a method for making the a-WO₃-gate ISFET.

Description of the prior art:

15 The ISFET was first disclosed by P. Bergveld in 1970. The device is a product of applied electrochemistry and microelectronics, and has the function of ion selection and the properties of the FET. This ion sensitive device is strictly different from the traditional ion selection
20 electrode. P. Bergveld disclosed a FET, wherein the metal film set in the gate of traditional FET was removed. Moreover, the device was dipped in electrolyte, wherein no reference electrode was present. However, it was found that a reference electrode must be added to determine the relative voltage
25 between the electrolyte and the semiconductor substrate during detecting so that the ISFET can be operated correctly.

Currently, a large amount of researches on ISFETs are underway. One interesting filed of the research is the use of the membrane for detection. When single gate detecting
30 membrane consists of silicon dioxide, the sensitivity and

stability of the device are poor. However, when the detecting membrane of the ISFET consists of double dielectric layers, such as $\text{Si}_3\text{N}_4/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Ta}_2\text{O}_5/\text{SiO}_2$, $\text{SnO}_2/\text{SiO}_2$ and a- WO_3/SiO_2 , the properties are superior to the ISFET with a
5 detecting membrane comprising a single SiO_2 gate. Regarding a H^+ -ISFET, it has been noted that a greater range of ions can be detected when a corresponding detecting membrane is covered on the SiO_2 or Si_3N_4 detecting membrane.

Today, the sorts of the FET based on ISFET process used
10 to detect ions and chemicals have reached more than 30. Moreover, the shrinking, integration, and multi-functionization of the ISFET devices have greatly progressed. The advantages of the ISFET can be summarized as follows:

1. Shrinkage size and micro-solution detectable;
- 15 2. High input resistance;
3. Low output resistance;
4. Fast reaction time;
5. Low price;
6. MOSFET processes compatible; and
- 20 7. Biosensor applicable.

Current ISFET researches can be classified into six categories:

1. Preparation of sensing membrane by CVD, thermal oxidation, E-gun evaporation, thermal evaporation and
25 sputtering;
2. Shrinkage of the device and the reference electrode;
3. Basic theory, such as site binding model;
4. Packing technique, such as packing material, for example Si-rubber and epoxy;
- 30 5. Integration of the devices and circuits; and

6. Simulation of the ISFETs.

A number of patents relating to ISFETs have been obtained, as summarized hereinafter. U.S. Patent No. 4,358,274 discloses a method and device
5 for compensating temperature-dependent characteristics change in ion-sensitive FET transducer, which is characterized by using a differential system consisting of ISFETs and a circuits-readout module. U.S. Patent No. 4,609,932
10 discloses a nonplanar ion-sensitive field-effect transistor device, which is characterized by forming a 3-D ISFET device by laser drilling and solid-state diffusion. U.S. Patent No. 4,657,658 discloses a semiconductor integrated circuit for
15 sensing a physico-chemical property of an ambient and includes a pair of semiconductor devices having a similar geometric and physical structure, one device being sensitive to the property, the other being insensitive to the property, together with a
20 differential amplifier having feedback connection to one of the pair of semiconductor devices. U.S. Patent No. 4,812,220 discloses an enzyme sensor for determining a concentration of glutamate, comprising an immobilize enzyme acting specifically
25 to a substrate and a transducer for converting the quantitative change of a substance or heat which is produced or consumed during an enzyme reaction to an electrical signal, wherein the enzyme is glutamine synthetase and the transducer is the pH
30 glass electrode or ion-sensitive field-effect

transistor (ISFET). The enzyme sensor can be miniaturized and can accurately determine a concentration of glutarate even when it is low. U.S. Patent No. 4,839,000 discloses buffer compensation in

5 enzyme-modified ion sensitive devices, which is characterized by using enzyme-modified ion sensitive field transistors to control the compensation of the ions in solution. U.S. Patent No. 5,319,226 discloses a method of fabricating an ion sensitive field effect transistor with a

10 Ta₂O₅ hydrogen ion sensing membrane, wherein a Ta₂O₅/Si₃N₄/SiO₂ dielectric layer, used as the sensor-device, is formed over the gate region of the ion sensitive field effect transistor by RF-sputtering. U.S. Patent No. 5,350,701 discloses a process for producing a surface gate of an integrated

15 electro-chemical sensor, and the integrated chemical sensor thus produced, wherein the surface gate is particularly sensitive to alkaline-earth species, and more particularly, sensitive to the calcium ion. U.S. Patent NO. 5,387,328 discloses a bio-sensor using ion sensitive field effect

20 transistor with platinum, wherein an immobilize enzyme membrane is immobilized on the ion-sensing film to determine the concentration of glucose. Moreover, a Pt reference electrode is introduced to shrink the size of the bio-sensor. U.S. Patent No. 5,407,854 disclose the ESD protection of

25 ISFET sensors, which is characterized by providing a method for providing electrostatic discharge protection to ion sensitive field effect transistor.

There has been interest in the material of the sensing membrane of ISFET, wherein a-WO₃ is a potential for use as

30 the gate of the ISFET. The a-WO₃ is a N-type semiconductor

compound, and has both wide energy gap ($E_g=2.1\sim 3.8$ eV) and high dielectric constant ($\epsilon=260 \epsilon_0$). Moreover, a- WO_3 is redox reversible, electrochromic and photochromic. Because the range of the resistivity of a- WO_3 is large (ranging from 10^{-3} to $10^{11} \Omega\cdot\text{cm}$), the a- WO_3 has potential to be a sensor, such as a gas sensor for detecting the CO_2 , NO_2 , H_2S , and so on.

Currently, a WO_3 layer can be formed by E-beam evaporation, DC or AC sputtering, thermal evaporation, vacuum evaporation, and CVD. The composition of the WO_3 layer and its properties vary with the selected method and condition during preparing the WO_3 layer. Most of the WO_3 layers are amorphous, polycrystalline or crystalline. The composition and structure of the WO_3 layer will directly affect its resistivity and electrochromic property; thereby the properties of the devices are determined by the composition and structure of the WO_3 layer.

In general, the composition of the WO_3 layer is hard to control regardless of which method is used in its formation. For example, the composition of the WO_3 layer made by vacuum evaporation is hard to control and the surface of the WO_3 layer is not uniform.

Some patents about the usage of ISFET have been disclosed using a H^+ -FET sensing film including SiO_2 , Si_3N_4 , Al_2O_3 , and Ta_2O_5 . However, a FET used to detect the industrial effluent is seldom mentioned, and especially a FET used to detect the effluent of low pH. Moreover, the gate of the conventional ISFET consists of a single SiO_2 layer; thereby the sensitivity and linearity cannot meet the practical requirements.

SUMMARY OF THE INVENTION

One feature of the invention discloses an ISFET comprising a H^+ -sensing material consisting of $a-WO_3$. The present ISFET is very sensitive in solution, and particularly
5 in acidic solution. The sensitivity of the ISFET of the present invention ranges from 50 to 58 mV/pH. In addition, the disclosed ISFET has high linearity. Accordingly, the ISFET of the present invention is suitable applied to detect effluent.

10 In order to achieve the above-mentioned feature, the present invention discloses a RF-sputtering $a-WO_3$ gate ISFET and the making thereof. This invention is characterized by forming the $a-WO_3$ layer as the sensing membrane of the ISFET by RF-sputtering, wherein the reactant consists of Ar and O_2 .
15 That is, the gate of the detecting device consists of $a-WO_3$ layer/ SiO_2 layer. Comparing the sensitivity of the sensing membrane in aqueous solution with various pH values, the results indicate the device made according to this invention is sensitive to the acidic aqueous solution and has good
20 linearity. Accordingly, the detecting device according to this invention is superior to the traditional detecting device containing a gate consisting of a single SiO_2 layer.

Other feature and advantages of the invention will be apparent from the following detailed description, and from
25 the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given hereinbelow
30 and the accompanying drawings, given by way of illustration

only and thus not intended to be limitative of the present invention.

Fig. 1a~1c are cross-sectional views of the processes according to the preferred embodiment of the invention.

5 Fig. 2 shows the EIS structure consisting of a-
WO₃/SiO₂.

Fig. 3 is a cross-sectional view of an ISFET with a gate consisting of a-WO₃/SiO₂.

10 Fig. 4 is a schematic cross-sectional view of a
capacitance-voltage measuring system.

Fig. 5 is the schematic cross-sectional view of an ISFET current-voltage measuring system.

15 Fig. 6 shows the capacitance-voltage curves of the
a-WO₃/SiO₂ gate EIS structure under various pH values (1, 3,
5, 7).

Fig. 7 shows the current-voltage curves of the SiO₂-gate ISFET under various pH values (2, 4, 6, 8, 10).

Fig. 8 shows the current-voltage curves of the SiO₂-gate ISFET under various pH values (2, 4, 6, 8, 10).

20 Fig. 9 shows the current-voltage curves of the a-
WO₃/SiO₂ gate ISFET under various pH values (1, 3, 5, 7).

Fig. 10 shows the current-voltage curves of the a-WO₃/SiO₂ gate ISFET under various pH values (1, 3, 5, 7).

25 Fig. 11 shows the sensitivity of the a-WO₃/SiO₂ gate
ISFET under various pH values (1, 3, 5, 7).

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an a-WO₃ gate ISFET device comprising: a semiconductor substrate; a gate oxide
30 layer on the semiconductor substrate; an a-WO₃ layer

overlying the gate oxide layer to form an a-WO₃ gate; a source/drain in the semiconductor substrate beside the a-WO₃ gate; a metal wire on the source/drain; and a sealing layer overlying the metal wire, and exposing the a-WO₃ layer.

5 In an embodiment of the present invention, the length of the channel, the width of the channel and ratio of width/length of the channel of the ISFET are 50μm, 1000μm and 20, respectively. The semiconductor substrate is P-type with a resistivity ranging from 8 to 12 Ω·cm. Moreover, the
10 lattice parameter of the semiconductor is (1,0,0). The thickness of the gate oxide is about 1000Å, and the thickness of the tungsten oxide layer is at least 1000Å. The metal wire consists of Al. The sealing layer consists of epoxide resin. The source/drain is N-type, which may consists of
15 phosphorous.

The present invention also provides a method for fabricating an a-WO₃ gate ISFET device, comprising the following steps: providing a semiconductor substrate; forming an imaginary gate on the semiconductor substrate to
20 define a gate area of the ISFET; forming a source/drain in the semiconductor substrate beside the imaginary gate; removing the imaginary gate; and forming an a-WO₃ gate in the gate area to form an ISFET.

In an embodiment of the present invention, the
25 semiconductor substrate is P-type with a resistivity of the semiconductor substrate ranges from 8 to 12 Ω·cm. Moreover, the lattice parameter of the semiconductor is (1,0,0). The imaginary gate consists of silicon dioxide with a thickness about 5000Å. In addition, the imaginary gate is removed by
30 wet-etching.

The step for forming an imaginary gate in the semiconductor gate to define a gate area of the ISFET, comprises: cleaning the semiconductor substrate; forming a pad oxide layer on the semiconductor substrate; and removing
5 a portion of the pad oxide layer to form an imaginary gate to define the area of the gate.

In the above-mentioned step for forming an imaginary gate in the semiconductor gate, the pad oxide layer can be formed by wet-oxidation. Additionally, the step of removing
10 a portion of the pad oxide layer can be completed by wet etching.

The step of forming a source/drain beside the imaginary gate comprises doping the semiconductor substrate by using the imaginary gate as a mask to form a source/drain,
15 wherein the dose of the dopants is about 10^{15} atoms/cm².

The step of forming an amorphous tungsten oxide gate in the gate area comprises: forming a gate oxide layer on the gate area, and forming an amorphous tungsten oxide layer to form the amorphous tungsten oxide gate, wherein the gate
20 oxide consists of silicon oxide with a thickness of about 1000Å. In addition, the amorphous tungsten oxide gate is formed by RF-sputtering.

The present invention also provides a method for fabricating an a-WO₃ gate ISFET device, comprising following
25 steps: providing a P-type semiconductor substrate; forming a pad oxide layer on the semiconductor layer; removing a portion of the pad oxide layer to form an imaginary gate to define a gate area; doping the semiconductor substrate using the imaginary gate as a mask to form a source/drain beside
30 the imaginary gate; removing the imaginary gate; forming a

gate oxide layer on the semiconductor substrate; and forming an a-WO₃ layer on the gate oxide layer to form an a-WO₃ gate.

In an embodiment of the above method, the resistivity of the semiconductor substrate ranges from 8 to 12 $\Omega \cdot \text{cm}$ and the lattice parameter of the semiconductor is (1,0,0). The thickness of the imaginary gate is about 5000Å. The pad oxide layer is formed by wet oxidation. The step of partially removing the pad oxide layer is performed by wet etching. The dopants used to dope the semiconductor substrate to form a source/drain beside the imaginary gate consist of phosphorous with a dosage of about 10^{15} atoms/cm². The imaginary gate is removed by wet etching. The gate oxide layer consists of silicon dioxide with a thickness of about 1000Å. The a-WO₃ layer is formed by RF-sputtering.

15

EMBODIMENT OF THE INVENTION

The ion sensitive field effect transistor (ISFET) according to the embodiment of this invention is illustrated in Fig. 1a~1b.

Referring to Fig. 1a, a P-type (1,0,0) semiconductor substrate 100 with a resistivity ranging from 8 to 12 $\Omega \cdot \text{cm}$ was provided. A pad oxide layer 102 consisting of silicon dioxide with a thickness of 5000Å was formed on the substrate 100 by wet-oxidation. A first photoresist pattern (non-shown) was formed on the pad oxide layer 102 by conventional photolithography. Using the photoresist pattern as a mask, a dummy gate 103 used to define the subsequent gate area was formed by removing a portion of the pad oxide layer 102.

Then, using the dummy gate 103 as a mask, impurities were implanted into the semiconductor substrate to form a

source/drain 104 beside the dummy gate 103. The impurities implanted herein were boron ions with a dose of 10^{15} cm^{-2} .

Referring to Fig. 1b, the dummy gate 103 was removed, that is the pad oxide layer 102 and the first photoresist pattern were removed by wet-etching. An insulating layer 106 consisting of silicon dioxide with a thickness of about 1000Å was formed on the semiconductor substrate 100. A second photoresist pattern (non-shown) was formed on the insulating layer 106 by photolithography. Then, using the second photoresist pattern as a mask, the insulating layer 106 outside the gate area was removed. The residual insulating layer within the gate area was used as a gate oxide layer. Subsequently, the second photoresist layer was removed.

An amorphous tungsten oxide layer 108 was formed on the insulating layer 106 by RF-sputtering. An amorphous tungsten oxide layer 108 with a thickness of at least 1000Å was sputtered on the insulating layer 106. Then a gate 109 consisting of the gate oxide layer 106 and the a-WO₃ layer 108 was generated. Thus, an a-WO₃ ISFET was obtained. The a-WO₃ ISFET had a channel length of about 50µm and a channel width of about 1000µm. Thus, the aspect ratio (i.e. channel width/channel length) of the present a-WO₃ ISFET was 20.

Referring to Fig. 1c, an interconnecting process was performed to obtain circuits of the ion sensitive field effect transistor (ISFET) using traditional interconnect steps for MOS. Therefore, an insulating layer 110 was formed on the source/drain 104, and a metal wire 112 was formed on the insulating layer 110 by etching and sputtering. Finally, a sealing layer 114 consisting of insulator was formed to seal the metal wire 112 except the amorphous tungsten oxide layer

108. The metal wire 112 consisted of aluminum, and the sealing layer 114 consists of epoxide resin.

Fig. 2 shows the scheme of the RF-sputtering a-WO₃/SiO₂ gated Electrolyte-Insulator-Semiconductor (EIS). As shown
5 in Fig. 2, the sensing membrane consists of the a-WO₃ layer.

Fig. 3 shows the cross-sectional view of a RF-sputtering a-WO₃ ISFET according to a preferred embodiment of the present invention. The structure of this ISFET is similar to that of MOSFET. The difference between the ISFET
10 and MOSFET is that the metal gate of the MOSFET is replaced by an a-WO₃ sensing membrane 35, an aqueous solution 36 and a reference electrode 38. The circuits were formed by contacting the metal wires 31, preferably consisting of Al, with source/drain 33. Since the sensing membrane 35 contacts
15 the detected solution 36, the whole device in addition to the sensing membrane 35 must be enclosed by a sealing layer 37 consisting of a material with good insulating property, such as epoxide resin. The reference electrode 38 was used to provide a detecting base.

20 The sensing membrane 35 of the ISFET is dipped into the detected solution 36 during operation, therefore the key point of the transformation from chemical equivalence to electrical equivalence within the ISFET is the contacting of the sensing membrane 35 and the aqueous solution 36. The
25 reaction mechanism of the ionic activity within the solution is the interface potential obtained from the interface between the aqueous solution 36 and the sensing membrane 35 dipped in the aqueous solution 35. The interface potential will vary with the ionic activities of various aqueous
30 solutions. In addition, the interface potential regulates

the channel conduction of the ISFET, which will result in the change of current within the source/drain 33.

Fig. 4 is the schematic cross-sectional view of the measuring system used to measure the capacitance and voltage of the device. The measurement is controlled by a computer 46 and analyzed by an inductance-capacitance-resistance analyzer 45 (HP 4284A). During measuring, the device 42 and reference electrode 43 are simultaneously put into a beaker 41 filled with aqueous solution 44. The detection is performed in a dark box 40 to reduce the effect caused by light.

Fig. 5 shows the cross-sectional view of a current-voltage measuring system of the ISFET according to the present invention. During measuring, the temperature of the aqueous solution was maintained by a temperature maintainer consisting of a P. I. D temperature controller 56, a heater 57 and a thermal couple 58. By placing the beaker 51 filled with full detected solution 54 on the container 59 of heater 57 in the bottom of this device, the temperature of the detected solution 54 was controlled through measuring the temperature of the detected solution 54 and maintained at a constant temperature. The aqueous solution was measured at room-temperature, therefore the temperature was set at 25 °C to avoid error caused by temperature variation. Moreover, a semiconductor parameter analyzer 55 was used to analyze the data.

Fig. 6 shows the capacitance-voltage curves of the RF-sputtering α -WO₃/SiO₂ gate EIS Structure in acidic solution with various pH values (1, 3, 5, 7), measured by an inductance-capacitance-resistance precision analyzer

(LCR Precision Analyzer, HP4284A), wherein the frequency was set at 100Hz. As shown in Fig. 6, the capacitance-voltage curves can be divided into an accumulation region I, an flat band region II, and an inversion region III. The C-V curves adequately shifted when the pH value of the aqueous solution changed. The sensitivity was calculated by placing the EIS in aqueous solutions with various pH values and measuring the shift voltage of the flat band region II. In addition, the curves locating in the flat band region shifted linearly with the change of solution.

The main reason for the capacitance-voltage curve to rightward shift with the increasing pH value is that the increased pH value will lower the concentration of hydrogen ions, thereby the potential of the surface of the sensing membrane will be reduced. Therefore, the positive carriers within the oxide layer move to the surface of the sensing membrane. High voltage is needed to force the positive carriers to move into the inside of the oxide layer. Accordingly, the capacitance-voltage curve shifts rightward when pH value increases.

Fig. 7 shows the current-voltage curves of aqueous solutions with various pH values (2, 4, 6, 8, 10) measured by the single gate ISFET, using SiO_2 as the sensing material, under room temperature. A semiconductor parameter analyzer (Model HP 4145B) was used to analyze the data. As shown in Fig. 7, the channel current of the device decreased with the increasing pH value; that's to say, the channel current of the ISFET changed with the hydrogen ions in the aqueous solution. According to the obtained results, when the ion sensor consists of SiO_2 , the current changes non-linearly,

and the variation increases with the increasing pH value.

Fig. 8 shows the current-voltage curves of the aqueous solutions with various pH values (2, 4, 6, 8, 10) measured by the single gate ISFET, using SiO_2 as the sensing membrane, under room-temperature. A semiconductor parameter analyzer (Model HP 4145B) was used to analyze the obtained data. As shown in Fig. 8, the threshold voltage increased with the increasing pH value. Consequently, the variation of the threshold voltage of the ISFET (i.e. the sensitivity of the sensor: S) in aqueous solutions with various pH values can be calculated. The definition of S is:

$$S = \Delta V_{th} / \Delta \text{pH} \text{ (mV/pH)}$$

wherein, ΔV_{th} is the variation of threshold voltage of the ISFET in the solution with various pH values (ΔpH).

According to the obtained results, the linearity and sensitivity of the single SiO_2 -gated sensor were poor, wherein the average sensitivity of the single SiC_2 gated sensor was about 32.3 mV/pH under ranging pH=2 to pH=10.

Fig. 9 shows the current-voltage curves of the RF-sputtering a- WO_3/SiO_2 gated ISFET fabricated according to this invention, wherein the measurement was accomplished by placing the sensing device in the acidic aqueous solutions (pH=1, 3, 5, 7) under room temperature. Similarly, the obtained data were analyzed by the semiconductor parameter analyzer (Model HP 4145B). According to Fig. 9, it was found that the channel current changed with the concentration of the hydrogen ions and the channel current linearly decreased with the increasing pH value of the aqueous sample when a- WO_3 sensing membrane was used.

Fig. 10 shows the current- voltage curves of the

RF-sputtering a-WO₃/SiO₂ gate ISFET fabricated according to this invention, wherein the measurement was accomplished by placing the sensing device in the acidic aqueous solutions (pH=1, 3, 5, 7) under room temperature. Similarly, the
5 obtained data were analyzed by the semiconductor parameter analyzer (Model HP 4145B). According to Fig. 10, it was found that the threshold voltage linearly increased with the increasing pH value of the aqueous solution when a-WO₃ sensing membrane was used.

10 Fig. 11 shows the sensitivity of the a-WO₃/SiO₂ gate ISFET fabricated according to this invention under various pH values (1, 3, 5, 7). As shown in the Fig. 11, the slope of the curve demonstrated the sensitivity of the sensing device. Accordingly, the sensitivity of the sensing device
15 consisting of a-WO₃/SiO₂ was 50 mV/pH.

Moreover, Table 1 shows the sensitivity of the a-WO₃/SiO₂-gate ISFET measured in acidic aqueous solutions (pH=1~5). As shown in Table 1, the sensitivity of the a-WO₃/SiO₂-gate ISFET measured in acidic aqueous solutions
20 (pH=1~5) ranged from 50~58mV/PH, and the sensitivity had no relationship to the thickness of the a-WO₃ sensing membrane. Thereby, the thickness of the sensing membrane will not affect the sensitivity of the sensing device.

25 Table 1. Sensitivity of the ISFET with different thickness of a-WO₃/SiO₂ gate under pH=1~5

Thickness (Å)	900	1400	2050	2200	2300	2500	3100	3300
Sensitivity (mV/pH)	50	54	53	52	58	55	54	53

The sensitivities of a-WO₃/SiO₂-gate ISFET, SiO₂-gate ISFET, Si₃N₄/SiO₂-gate ISFET, Al₂O₃/SiO₂-gate and Ta₂O₅/SiO₂-gate ISFET were compared. The results were shown in Table 2. As shown in Table 2, it was noted that the sensitivity and the linearity of the double layer-gate ISFETs were higher than those of the single SiO₂-gate ISFET. In addition, the RF-sputtering a-WO₃ was superior to the above-mentioned materials on the SiO₂ layer when ISFET was used to detect acidic aqueous solution. The sensitivity of the a-WO₃/SiO₂-gate ISFET ranged from 50 to 58 mV/pH under pH=1~5.

Table 2

Material	SiO ₂	Si ₃ N ₄ / SiO ₂	Al ₂ O ₃ / SiO ₂	Ta ₂ O ₅ / SiO ₂	a-WO ₃ /SiO ₂
Testing range (pH value)	2~10	1~13	1~13	1~13	1~5
Sensitivity (mV/pH)	32~33	46~56	53~57	56~57	50~58
Linearity	Bad	Good	Good	Good	Good

As above-mentioned description, the advantages of the amorphous tungsten oxide ISFET according to this invention include:

1. The a-WO₃/SiO₂-gate ISFET according to this invention is formed by replacing the traditional metal layer existing in the gate of FET with a RF-sputtering a-WO₃ membrane. In addition to being easy to produce, other advantages include high input resistance, low output resistance, short reaction time, trace detectable, and MOS processes compatibility.

2. The gate of the ISFET is double layer consisting of α - WO_3/SiO_2 , which is sensitive when used to detect an acidic aqueous solution. Accordingly, this α - WO_3/SiO_2 -gate ISFET can be applied to monitor and detect the industrial effluent, and particularly acidic effluent. Since the ISFET is trace detectable, it can be used as a bio-sensor.

3. Since α - WO_3 is used as the material of the sensing membrane for detecting hydrogen ions, and the MOS structure is used, the H^+ -detecting device has both the properties of MOS and excellent H^+ -detecting ability.

The foregoing description of the preferred embodiments of this invention has been presented for purposes of illustration and description. Obvious modifications or variations are possible in light of the above teaching. The embodiments were chosen and described to provide the best illustration of the principles of this invention and its practical application to thereby enable those skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the present invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally, and equitably entitled.

WHAT IS CLAIM IS:

1 1. An a-WO₃ gate SFET device, comprising:
2 a semiconductor substrate;
3 a gate oxide layer on the semiconductor substrate;
4 an a-WO₃ layer overlying the gate oxide layer to form
5 an a-WO₃ gate;
6 a source/drain in the semiconductor substrate beside
7 the a-WO₃ gate;
8 a metal wire on the source/drain; and
9 a sealing layer overlying the metal wire, and
10 exposing the a-WO₃ layer.

1 2. The device as claimed in claim 1, wherein the
2 length of the channel, the width of the channel and ratio of
3 width/length of the channel of the ISFET is about 50μm, 1000μm,
4 and 20 respectively.

1 3. The device as claimed in claim 1, wherein the
2 semiconductor substrate is P-type.

1 4. The device as claimed in claim 1, wherein the
2 resistivity of the semiconductor substrate ranges from 8 to
3 12 Ω·cm.

1 5. The device as claimed in claim 1, wherein the
2 lattice parameter of the semiconductor is (1,0,0).

1 6. The device as claimed in claim 1, wherein the
2 thickness of the gate oxide is about 1000Å.

1 7. The device as claimed in claim 1, wherein the
2 thickness of the tungsten oxide layer is at least 1000Å.

1 8. The device as claimed in claim 1, wherein the metal
2 wire consists of Al.

1 9. The device as claimed in claim 1, wherein the
2 sealing layer consists of epoxide resin.

1 10. The device as claimed in claim 1, wherein the
2 source/drain is N-type.

1 11. The device as claimed in claim 10, wherein the
2 N-type impurities within the source/drain consist of
3 phosphorous.

1 12. A method for fabricating an a-WO₃ gate ISFET
2 device, comprising the following steps:
3 providing a semiconductor substrate;
4 forming an imaginary gate on the semiconductor
5 substrate to define the gate area of the ISFET;
6 forming a source/drain in the semiconductor
7 substrate beside the imaginary gate;
8 removing the imaginary gate; and
9 forming an a-WO₃ gate in the gate area to form a ISFET.

1 13. The method as claimed in claim 12, wherein the
2 semiconductor substrate is P-type.

1 14. The method as claimed in claim 12, wherein the

2 resistivity of the semiconductor substrate ranges from 8 to
3 12 $\Omega \cdot \text{cm}$.

1 15. The method as claimed in claim 12, wherein the
2 lattice parameter of the semiconductor is (1,0,0).

1 16. The method as claimed in claim 12, wherein the
2 imaginary gate consists of silicon dioxide.

1 17. The method as claimed in claim 12, wherein the
2 thickness of the imaginary gate is about 5000Å.

1 18. The method as claimed in claim 12, wherein the
2 imaginary gate is removed by means of wet-etching.

1 19. The method as claimed in claim 12, wherein the
2 step of forming an imaginary gate in the semiconductor gate
3 to define a gate area of the ISFET comprises:

4 cleaning the semiconductor substrate;

5 forming a pad oxide layer on the semiconductor
6 substrate; and

7 removing a portion of the pad oxide layer to form an
8 imaginary gate to define the area of the gate.

1 20. The method as claimed in claim 19, wherein the
2 pad oxide layer is formed by means of wet oxidation.

1 21. The method as claimed in claim 19, wherein the
2 step of removing a portion of the pad oxide layer is completed
3 by means of wet etching.

1 22. The method as claimed in claim 12, wherein the
2 step of forming a source/drain beside the imaginary gate
3 comprises:

4 doping the semiconductor substrate by using the
5 imaginary gate as a mask to form a source/drain.

1 23. The method as claimed in claim 22, wherein the
2 dose of the dopants is about 10^{15} atoms/cm².

1 24. The method as claimed in claim 12, wherein the
2 step of forming an a-WO₃ gate in the gate area comprises:
3 forming a gate oxide layer on the gate area; and
4 forming an a-WO₃ layer on the gate oxide to form a a-WO₃
5 gate.

1 25. The method as claimed in claim 24, wherein the
2 thickness of the gate oxide layer is about 1000Å.

1 26. The method as claimed in claim 24, wherein the
2 gate oxide consists of silicon dioxide.

1 27. The method as claimed in claim 24, wherein the
2 a-WO₃ gate is formed by RF-sputtering.

1 28. A method for fabricating an a-WO₃ gated ISFET,
2 comprising following steps:
3 providing a P-type semiconductor substrate;
4 forming a pad oxide layer on the semiconductor layer;
5 removing a portion of the pad oxide layer to form an
6 imaginary gate to define a gate area;

7 doping the semiconductor substrate by using the
8 imaginary gate as a mask to form a source/drain beside the
9 imaginary gate;
10 removing the imaginary gate;
11 forming a gate oxide layer on the semiconductor
12 substrate; and
13 forming an a-WO₃ layer on the gate oxide layer to form
14 an a-WO₃ gate.

1 29. The method as claimed in claim 28, wherein the
2 resistivity of the semiconductor substrate ranges from 8 to
3 12 $\Omega \cdot \text{cm}$.

1 30. The method as claimed in claim 28, wherein the
2 lattice parameter of the semiconductor is (1,0,0).

1 31. The method as claimed in claim 28, wherein the
2 thickness of the imaginary gate is about 5000Å.

1 32. The method as claimed in claim 12, wherein the
2 pad oxide layer is formed by means of wet oxidation.

1 33. The method as claimed in claim 28, wherein the
2 step of partially removing the pad oxide layer is performed
3 by wet etching.

1 34. The method as claimed in claim 28, wherein the
2 dopants used for doping consist of phosphorous.

1 35. The method as claimed in claim 28, wherein the

2 dose of the dopants is 10^{15} atoms/cm².

1 36. The method as claimed in claim 28, wherein the
2 imaginary gate is removed by wet etching.

1 37. The method as claimed in claim 28, wherein the
2 gate oxide layer consists of silicon dioxide.

1 38. The method as claimed in claim 28, wherein the
2 thickness of the gate oxide layer is about 1000Å.

1 39. The method as claimed in claim 28, wherein the
2 a-WO₃ layer is formed by RF-sputtering.

ABSTRACT of the DISCLOSURE

Disclosed is an ISFET comprising a H^+ -sensing membrane consisting of RF-sputtering $\alpha-WO_3$. The $\alpha-WO_3/SiO_2$ -gate ISFET of the present invention is very sensitive
5 in aqueous solution, and particularly in acidic aqueous solution. The sensitivity of the present ISFET ranges from 50 to 58 mV/pH. In addition, the disclosed ISFET has high linearity. Accordingly, the disclosed ISFET can be used to detect effluent.

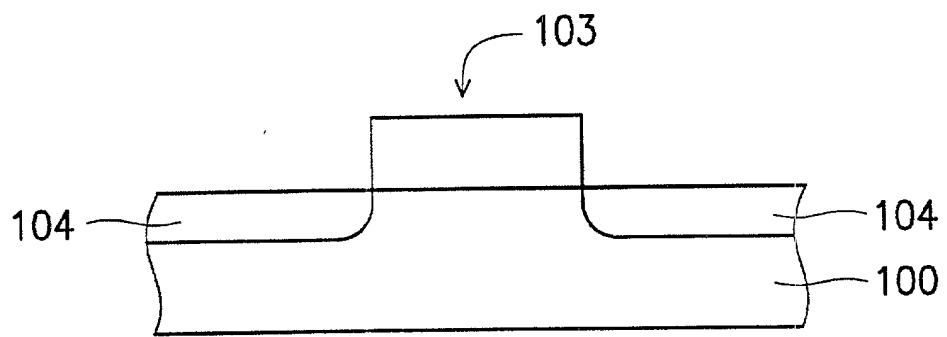


FIG. 1a

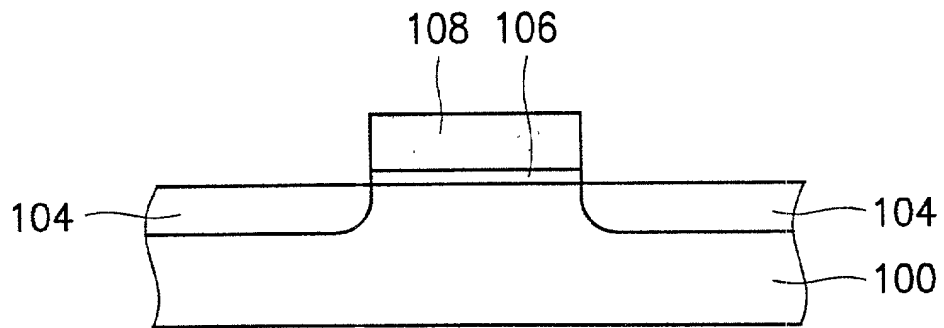


FIG. 1b

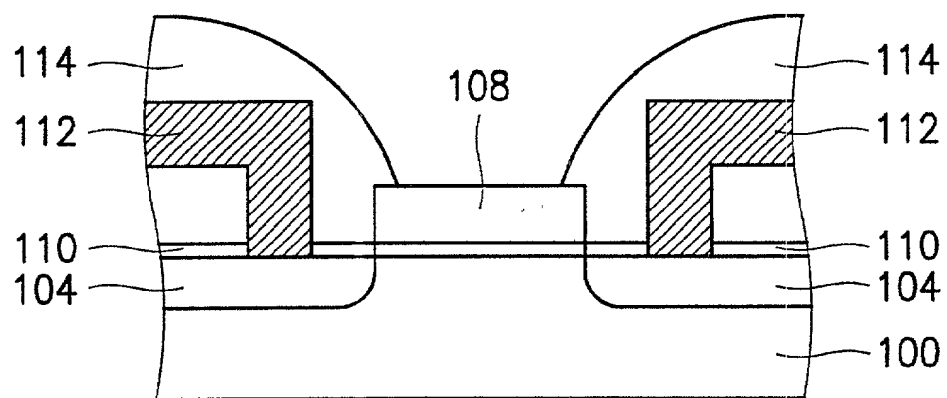


FIG. 1c

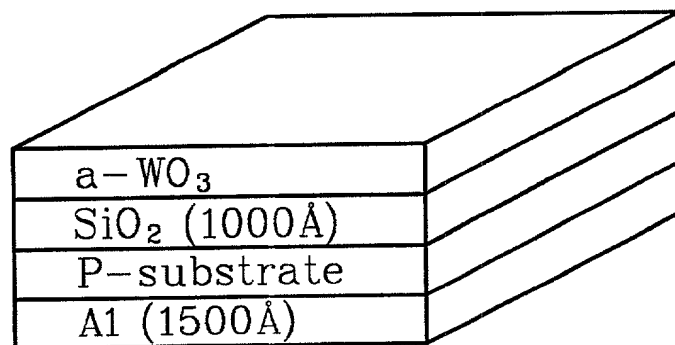


FIG. 2

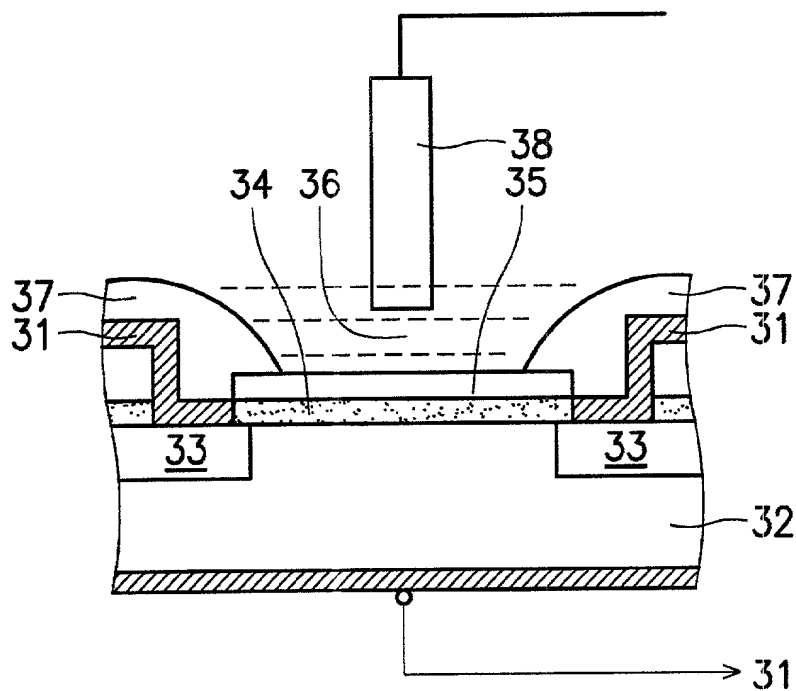


FIG. 3

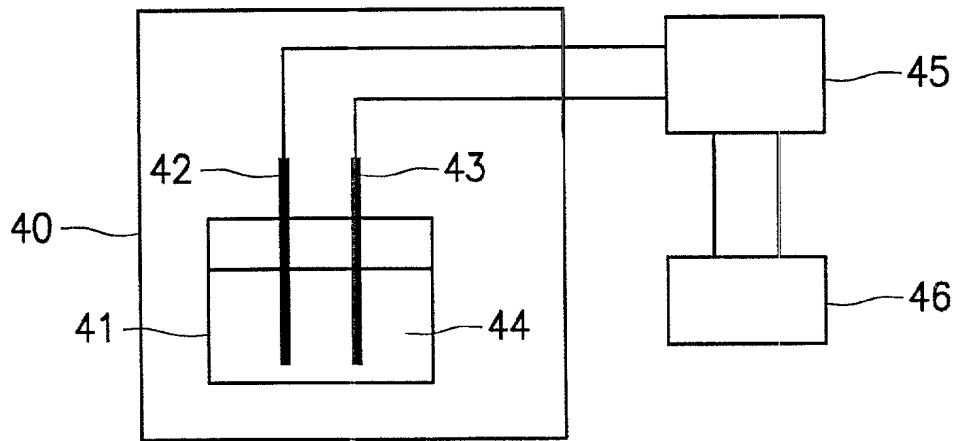


FIG. 4

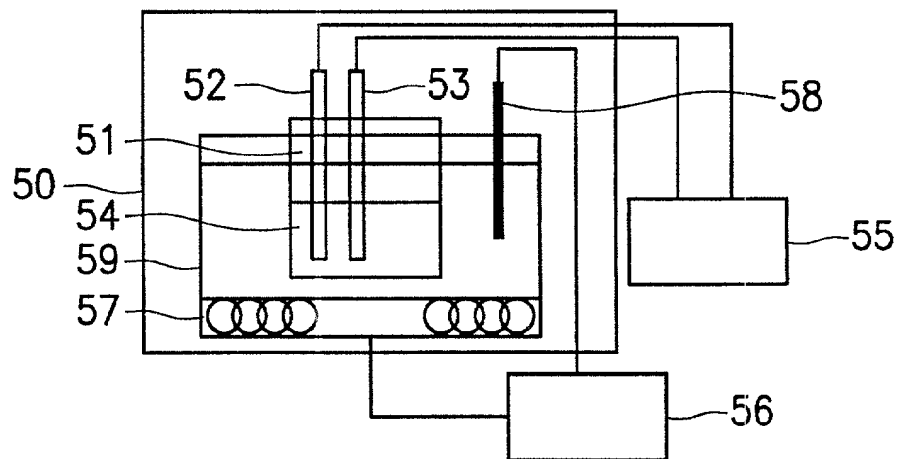


FIG. 5

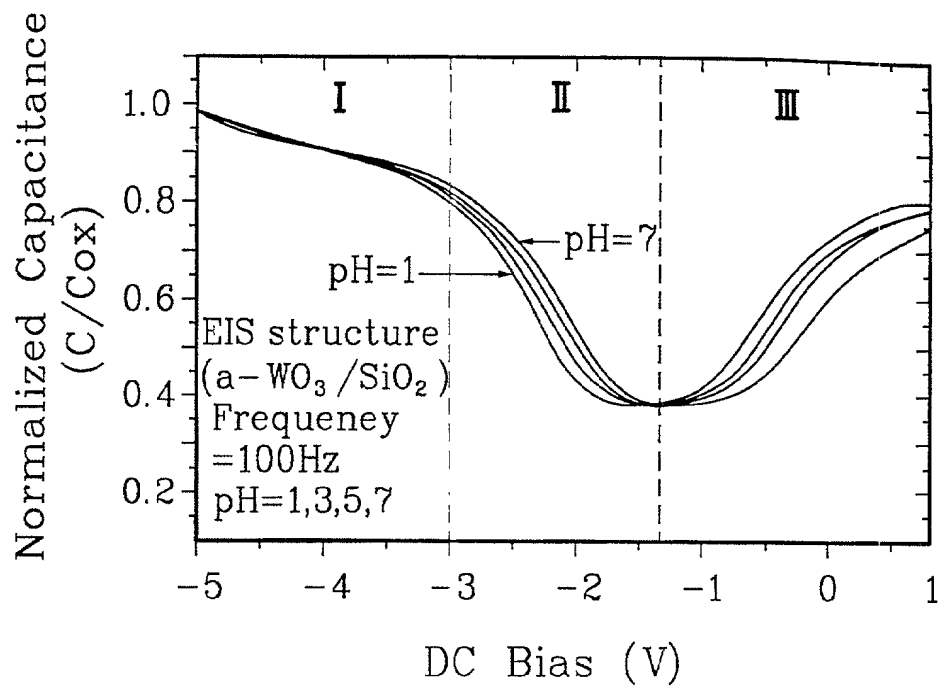


FIG. 6

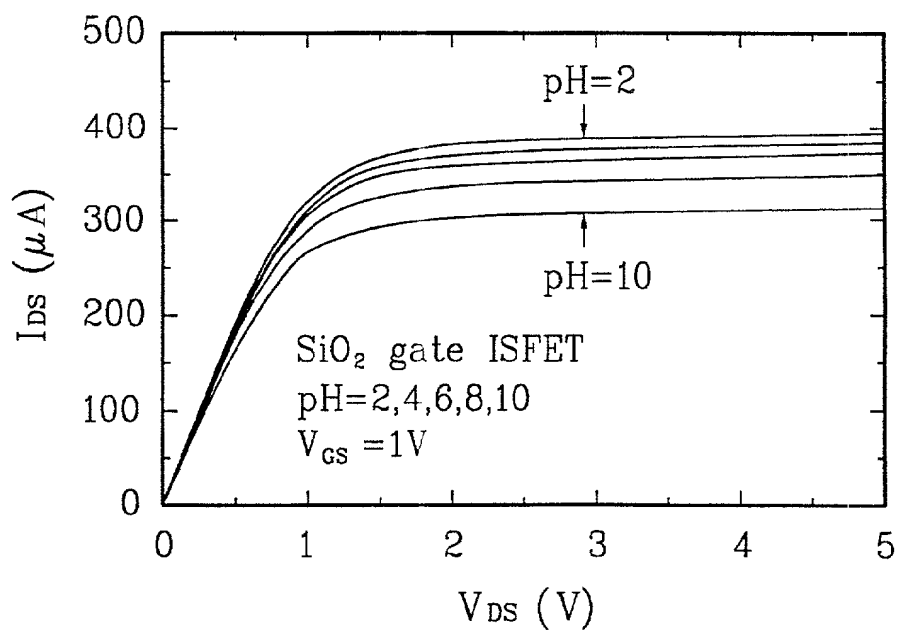


FIG. 7

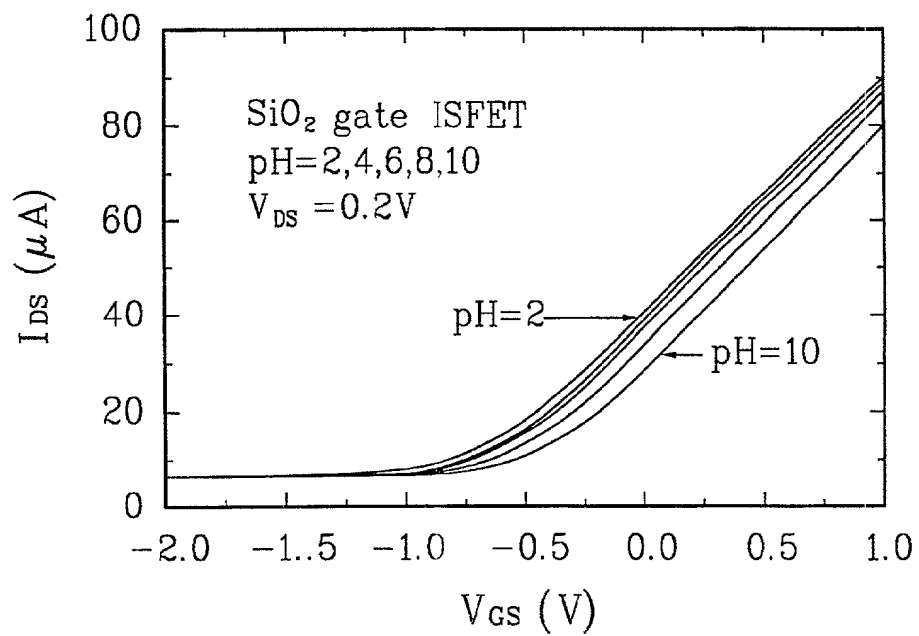


FIG. 8

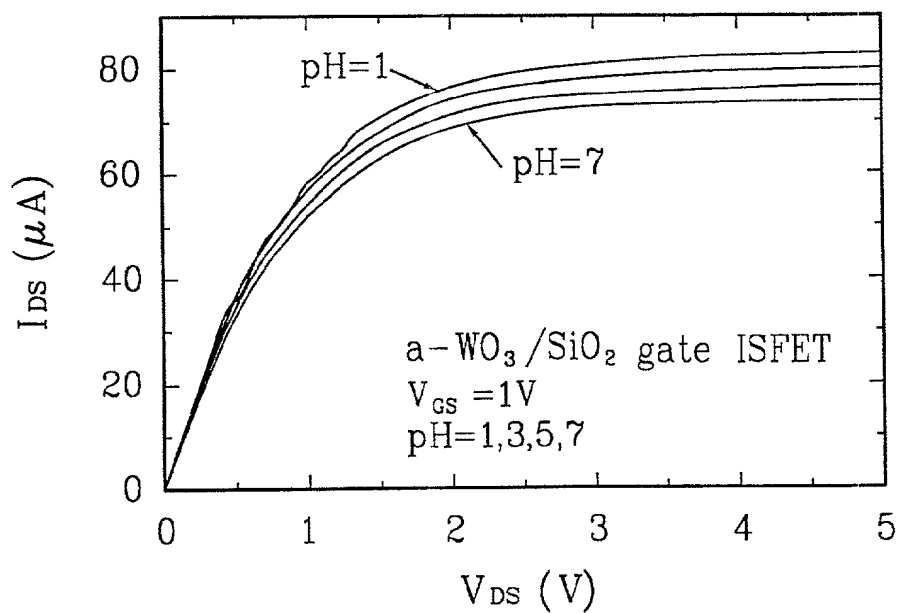


FIG. 9

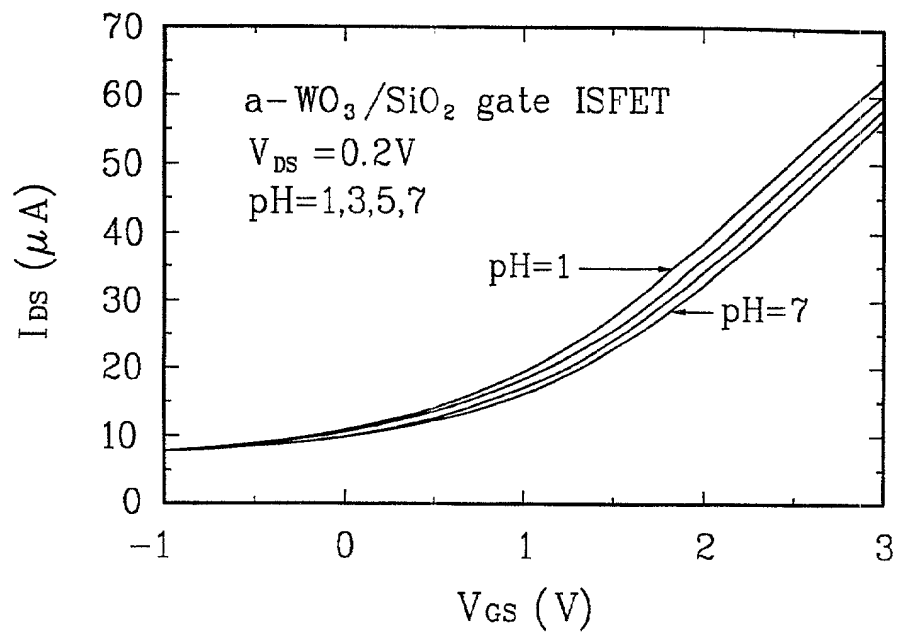


FIG. 10

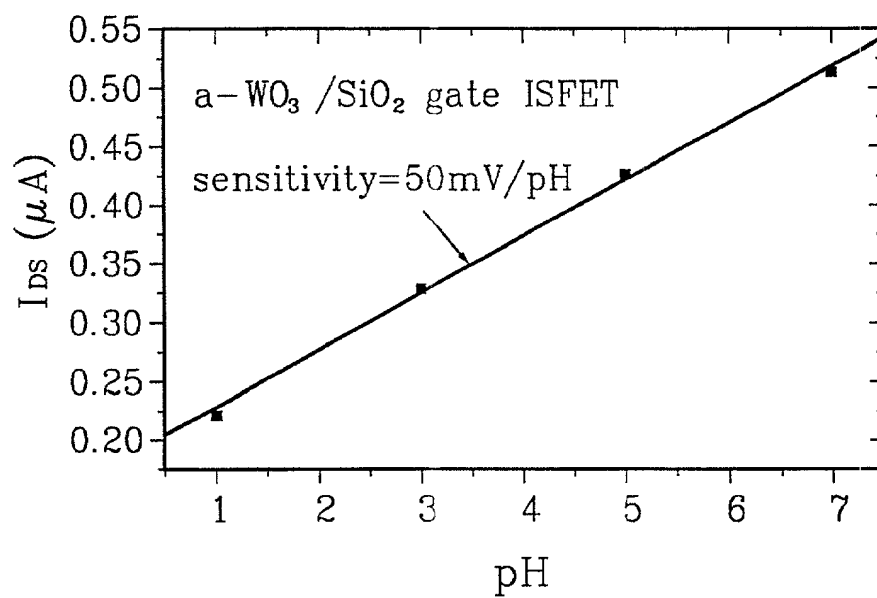


FIG. 11

Declaration for U.S. Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
(Insert Title) a-WO3-GATE ISFET DEVICES AND METHOD OF MAKING THE SAME
the specification of which is attached hereto unless the following is checked



was filed on _____ as United States Application Number or PCT International Application Number
and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application for which priority is claimed:

Priority Claimed

(List prior
foreign
applications.
See note A on
back of this
page)

88109799

(Number)

Taiwan, R.O.C. 11/06/1999

(Country)

(Day/Month/Year Filed)

☒ Yes ☐ No

(Number)

(Country)

(Day/Month/Year Filed)

☐ Yes ☐ No

(Number)

(Country)

(Day/Month/Year Filed)

☐ Yes ☐ No

(Number)

(Country)

(Day/Month/Year Filed)

☐ Yes ☐ No

(See note B on back of this page)

☐ See attached list for additional prior foreign applications

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

(List Prior U.S.
Applications)

(Appln. Serial No.)

(Filing Date)

(Status: Patented, Pending, Abandoned)

(Appln. Serial No.)

(Filing Date)

(Status: Patented, Pending, Abandoned)

(Appln. Serial No.)

(Filing Date)

(Status: Patented, Pending, Abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Raymond J. Ho, Reg. No. 41,838

Please direct all communications to the following address: INTELLECTUAL PROPERTY SOLUTIONS, P.L.L.C.
1300 Pennsylvania Avenue, N.W., Suite 700
Washington, D.C. 20004
Telephone: (202) 204-3080 Fax: (202) 204-3082

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18 of the United States Code, § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

(See note C above) Full name of sole or first inventor (given name, family name) Jung Chuan CHOU
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Inventor's signature Jung Lung Chiang Date February 29, 2000
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Full name of third inventor (given name, family name) _____
Inventor's signature _____ Date _____
Residence _____ Citizenship _____
Post Office Address _____

Full name of fourth inventor (given name, family name) _____
Inventor's signature _____ Date _____
Residence _____ Citizenship _____
Post Office Address _____

Full name of fifth inventor (given name, family name) _____
Inventor's signature _____ Date _____
Residence _____ Citizenship _____
Post Office Address _____

Full name of sixth inventor (given name, family name) _____
Inventor's signature _____ Date _____
Residence _____ Citizenship _____
Post Office Address _____

Full name of seventh inventor (given name, family name) _____
Inventor's signature _____ Date _____
Residence _____ Citizenship _____
Post Office Address _____

Full name of eighth inventor (given name, family name) _____
Inventor's signature _____ Date _____
Residence _____ Citizenship _____
Post Office Address _____